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(54) Title: CERAMIC DISHWASHING COMPOSITION

(57) Abstract: Use of a ceramic composition to protect glassware from corrosion, the ceramic composition being made using at least one compound which releases an active agent during washing and/or rinsing cycles of a dishwasher to protect glassware from corrosion.

CERAMIC DISHWASHING COMPOSITION

The invention relates to a new type of use for a ceramic composition to protect glassware from corrosion during washing and/or rinsing cycles of a dishwasher, compositions intended for use in a dishwasher for the aforesaid purpose and a method of inhibiting the corrosion of glassware during washing and/or rinsing cycles of a dishwasher.

The problem of glassware corroding during washing and/or rinsing cycles of a dishwasher has long been known. Current opinion is that the problem of corrosion in glassware is the result of two separate phenomena. On the one hand, the corrosion is clearly due to minerals from the glass composition accompanied by hydrolysis of the silicate network. On the other hand, silicate material is released from the glass. After several washes in a dishwasher, both phenomena can cause damage to glassware such as cloudiness, scratches, streaks and similar.

Silicate compounds are known to be effective in preventing minerals from being released from the glass composition but on the other hand can tend to increase the separation of silicate material at the surface of the glass.

Various proposals have been put forward as a means of dealing with the problems described above.

One approach is to use zinc, either in metallic form (US Patent No. 3,677,820) or in the form of zinc compounds. The use of soluble zinc salts as a means of preventing the corrosion of glassware in dishwasher cleansers is described in US Patent No. 3,255,117, for example.

Because of a number of disadvantages inherent in using soluble zinc salts (in particular the formation of a precipitate of insoluble zinc salts with other ions in the washing or rinsing water), European patent applications EP 0 383 480, EP 0 383 482 and EP 0 387 997 propose the use of insoluble zinc compounds as a means of inhibiting corrosion of glassware in automatic dishwashers. Specifically, the insoluble zinc salts proposed are zinc silicate, zinc carbonate, zinc oxide, basic zinc carbonate (approximately: $Zn_2(OH)_2CO_3$), zinc hydroxide, zinc oxalate, zinc monophosphate ($Zn_3(PO_4)_2$) and zinc pyrophosphate ($Zn2(P_2O7)$). If using zinc salts of this type in granular cleansing compounds, the insoluble zinc compound is specified as having a maximum particle size of less than 1.7 mm (EP 0 383 482), whilst a mean particle size of less than 250 µm is specified for the insoluble zinc compound used in a liquid dishwasher compound - (EP 0 383 480 and EP 0 387 997).

The disadvantage of the prior art essentially resides in the fact that, because the zinc compounds are not re2adily soluble or are insoluble, it is difficult to ensure that a sufficient quantity of active agent will be present in the washing or rinsing liquid to protect glassware from corrosion. Furthermore, in view of the

high specific density of the insoluble zinc compounds listed, problems of separation arise with powdered mixtures or settlement in the case of liquid mixtures. Finally, all of the known compositions are intended to be active during only one specific stage of the washing cycle, i.e. if admixed with a granular cleanser composition during the washing cycle or if admixed with a liquid rinsing composition with the rinsing cycle. None of the known compositions has the capacity to become and remain active starting from the washing cycle and/or one of the intermediate rinsing cycles onwards.

The underlying objective of the present invention is to resolve one but preferably all of the existing problems outlined above.

This objective is achieved by the invention due to the use of a ceramic composition to protect glassware from corrosion, the ceramic composition being made using at least one compound which releases an active anti-corrosion agent during the washing and/or rinsing cycles of a dishwasher.

By preference, the compound(s) which release(s) an active agent to prevent corrosion during washing and/or rinsing cycles of a dishwasher is/are from the group consisting of the oxides of zinc, aluminium, tin, magnesium, calcium, strontium, silicon, titanium, zirconium, manganese and/or lanthanum and/or precursors thereof.

In one specific embodiment, the invention proposes that at least one of the compounds used should be zinc oxide and/or a precursor thereof.

By preference, the ceramic composition is used in tablet form.

Alternatively, the ceramic composition is used in crushed form, and more preferably in ground form.

The ground ceramic composition preferably has an average particle size of at most 500 µm.

The invention also relates to a composition for use in a dishwasher which contains an active quantity of a ceramic composition in crushed form to protect glassware against corrosion, the ceramic composition being made using at least one compound which releases an active agent to protect glassware from corrosion during washing and/or rinsing cycles of a dishwasher.

The ceramic composition is preferably used in ground form, more preferably with a mean particle size of at most 500 µm.

The composition proposed by the invention preferably contains the crushed ceramic composition in a quantity of from 0.1 to 10.0% by weight, more preferably in a quantity of from 0.5 to 5.0% by weight.

The invention also relates to a composition for use in a dishwasher in the form of a tablet containing an

active quantity of a ceramic composition to protect glassware against corrosion, the ceramic composition being made using at least one compound which releases an active agent during washing and/or rinsing cycles of a dishwasher to protect glassware from corrosion.

In one embodiment, the invention proposes that the compound(s) which release(s) an active agent to protect glassware from corrosion during washing and/or rinsing cycles of a dishwasher should be selected from the group consisting of the oxides of zinc, aluminium, tin, magnesium, calcium, strontium, silicon, titanium, zirconium, manganese and/or lanthanum.

In one particular embodiment, the invention proposes that at least one of the compounds should be zinc oxide and/or a precursor thereof.

Finally, the invention relates to a method of inhibiting the corrosion of glassware during washing and/or rinsing cycles of a dishwasher, characterised in that the glassware is brought into contact with washing or rinsing water containing an active quantity of the aforesaid composition containing a crushed ceramic composition.

Alternatively, a method of inhibiting the corrosion of glassware during washing and/or rinsing cycles of a dishwasher is proposed, in which the composition described above containing the ceramic composition is provided in tablet form, placed in the interior of the

dishwasher at a point which is accessible to the washing and/or rinsing water.

Before giving a detailed explanation of the features and advantages of the present invention, it should be pointed out that for the purpose of the present invention, the concept "ceramic composition" should be construed in its broadest sense, namely all materials made up of inorganic and predominantly non-metallic compounds or elements that are crystalline by reference to more than 30% by volume, in particular - but not restricted to - clay ceramic substances but also glass ceramic substances, for example.

The present invention solves at least one, and in preferred embodiments all the problems inherent in the prior art described above.

By using a ceramic substance as a "base" for one or more reagents to protect glassware from corrosion in a dishwasher, the problem caused by the extensive formation of precipitate from insoluble salts which result in an undesirable deposit, such as occurs with the prior art due to the use of soluble zinc salts for this purpose, are avoided. Instead, the active agents, such as zinc ions, are released from the ceramic compound proposed by the invention into the washing or rinsing water in a delayed release pattern but are not present in a high enough concentration to lead to an extensive and undesirable formation of insoluble salts. The disadvantages of using insoluble zinc compounds described

above are avoided by using the ceramic compositions proposed by the invention.

By using the ceramic composition proposed by the invention in ground form as an additive to standard dishwasher products, which are generally made as powders or liquids, the problem of separation described above is also resolved since the use of a ceramic composition offers greater flexibility in terms of adjusting the specific density to requirements.

If the ceramic composition proposed by the invention is provided in tablet form and placed in the interior of the dishwasher at a point which is accessible to the washing and/or rinsing water, e.g. in the cutlery basket, it will also provide, for the first time ever, active protection against corrosion throughout all washing and rinsing cycles, i.e. from the pre-rinse cycle through to the cleaning cycle and then the intermediate rinse cycles through to the final rinse cycle and, what is more, will last for several cycles. As a result, not only is glassware thoroughly protected against corrosion in the dishwasher, handling is made significantly easier and more convenient for the consumer.

If the ceramic composition proposed by the invention is used in crushed form, it may be ground in a grinder specifically suited to this purpose, for example, and an appropriate fraction of particles separated out, e.g. having an average grain particle of at most 500 µm.

The features of the invention disclosed in the description above and in the claims may be used individually or in any combination to apply the invention in its different embodiments.

The invention will now be described with reference to the following examples.

Example 1

In this example a ceramic material with the composition of Table I was prepared using the process described below:

Table 1

Component	Mol %
P_2O_5	24
Na_2O	27
SiO_2	25
ZnO	24

Process of preparation:

45 g Na_3PO_4 anhydrous, 63 g NaH_2PO_4 , 21 g SiO2 and 77 g Zr_3PO_4 all anhydrous were homogeneously mixed and wetted with a small amount of water during steadily kneading of the mixture until a dough like plastic mass is obtained. The mass is left to stand for 2 hours at 30

°C during which time the mass swells due to the development of gas inside. The body is kneaded again to eliminate the gas and close the pores. The resulting mixture is fed into the die of a press machine having a rectangular cross-section of 8 x 8 cm^2. The mixture was pressed to obtain a block. The block dries in between 12 hours at 35 °C to a solid block.

The block was then placed in an electric oven, which was heated up to 150°C at a speed of 50°C/hour. Once the temperature of 150°C is reached the heating rate is increased to 180 °C/hour until a temperature of 780 °C is reached and this temperature is then maintained for 24 hours. After this period the oven is brought back to room temperature at a rate of 180°C/hour.

Example 2

Table 2

Component	Mol %
P_2O_5	25
Na_2O	30
SiO_2	15
ZrO_2	10
CaO	20

The preparation, processing, forming and sintering of this composition was made following the same process explained for Example 1.

Example 3

Comparative tests on the glass-protecting performance of the composition of Example 1 were performed as explained below.

Pieces of glassware where washed 50 and 100 times in a dishwashing machine (Miele G540) using for each cleaning cycle 20 g of the commercial dishwashing detergent "Calgonit Ultra 2-Phases Powder" and setting the machine to a program running at a 65°C in the washing cycle and at 65°C in the rinsing cycle. The water hardness in the dishwashing machine was set to be 0,1°dGH and the average water consumption per wash was 23,5 l. In the rinsing cycle the machine was set to use 3 ml of the commercial rinse aid "Calgonit Klarspüller".

The pieces of glassware used for the test were as follows:

Luigi Bormioli (Italy):

" linea Michelangelo David" C180, Stemglass, crystal glass

Verrerie Cristallerie D´Arques (France):

"Luminarc Octime Transparent", Whiskeyglass 30cl

"Longchamp" 17 cl; Stemglass, lead crystal glass

"Luminarc Islande Dauphine", 33 cl, decorated longdrinkglass

Ruhr Kristall Glas (Germany):

"Kölner Stange" ,24 cl, beer glass

New pieces of glassware were used for the test and each was weighted before the test started. After 50 or 100 complete washing cycles the pieces of glassware were removed from the dishwasher and their weight loss was determined gravimetrically.

Additionally the pieces of glassware were visually examined by a panel of trained people in two different environments: at daylight conditions and in a light chamber measuring 70 cm x 40 cm x 65 cm whose interior is covered with a matt black coating and which is illuminated with an Osram L20W25S lamp.

The results of the visual examination were recorded using the following scale:

Value	Evaluation at daylight	Evaluation in light chamber
0	No change	No change
1	No visible cloudiness	Slight cloudiness
2	Few visible cloudiness	Considerable cloudiness
3	Considerable visible cloudiness	Strong cloudiness
4	Strong cloudiness	-------

The results on glass corrosion of the glassware when no special glass-protecting composition is used are recorded under the heading "Reference". The results obtained when the ceramic composition prepared in Example 1 was placed in the interior of the dishwashing machine at the start of the test are recorded under the heading "Ceramic".

Gravimetrical determination of glass corrosion

	50 cycles		100 cycles	
Glassware type	Reference	Ceramic	Reference	Ceramic
Michelangelo	41	13	80	28
Octime	20	8	38	20
Longchamp	62	20	125	44
RKL Kölsch	25	5	44	14
Islande-Dekor	378	205	625	398

Visual determination of glass damages

	50 cycles		100 cycles	
	Reference	Ceramic	Reference	Ceramic
Michelangelo	2,5	1	3,5	1,5
Octime	2	0,5	3	1,5
Longchamp	3	1	3,5	1,5
RKL Kölsch	2	1	3	1,5
Islande-Dekor	2,5	1	3,5	2

The results from the preceding tables clearly show that the use of the ceramic compositions of the invention substantially reduces the corrosion of glassware when repeatedly washed in a dishwashing machine.

Claims

1. Use of a ceramic composition to protect glassware from corrosion, the ceramic composition being made using at least one compound which releases an active agent to protect glassware from corrosion during washing and/or rinsing cycles of a dishwasher.

2. Use as claimed in claim 1, characterised in that the compound(s) which release(s) an active agent to protect glassware from corrosion during washing and/or rinsing cycles of a dishwasher is/are selected from the group consisting of oxides of zinc, aluminium, tin, magnesium, calcium, strontium, silicon, titanium, zirconium, manganese and/or lanthanum and/or precursors thereof.

3. Use as claimed in claim 2, characterised in that at least one of the compounds is zinc oxide and/or a precursor thereof.

4. Use as claimed in one of the preceding claims, characterised in that the ceramic composition is used in tablet form.

5. Use as claimed in one of claims 1 to 3, characterised in that the ceramic composition is used in crushed form.

6. Use as claimed in claim 5, characterised in that the ceramic composition is used in ground form.

7. Use as claimed in claim 6, characterised in that the ground ceramic composition has an average particle size of at most 500 µm.

8. Composition for use in a dishwasher, characterised in that it contains an active quantity of a ceramic composition in ground form to protect glassware from corrosion, the ceramic composition being made using at least one compound which releases an active agent during washing and/or rinsing cycles of a dishwasher to protect glassware from corrosion.

9. Composition as claimed in claim 8, characterised in that the ceramic composition is provided in ground form.

10. Composition as claimed in claim 9, characterised in that the ground ceramic composition has an average particle size of at most 500 µm.

11. Composition as claimed in one of claims 8 to 10, characterised in that the crushed, ceramic compound is present in a quantity of from 0.1 to 10.0 by weight.

12. Composition as claimed in claim 11, characterised in that the crushed ceramic compound is present in a quantity of from 0.5 to 5.0% by weight.

13. Composition for use in a dishwasher, characterised in that it contains an active quantity of a ceramic composition in tablet form to prevent the corrosion of glassware, the ceramic composition being made using at least one compound which releases an active agent during

washing and/or rinsing cycles in a dishwasher to protect glassware from corrosion.

14. Composition as claimed in one of claims 8 to 13, characterised in that the compound(s) which release(s) an active agent during washing and/or rinsing cycles of a dishwasher to protect glassware from corrosion is/are selected from the group consisting of the oxides of zinc, aluminium, tin, magnesium, calcium, strontium, silicon, titanium, zirconium, manganese and/or lanthanum.

15. Composition as claimed in claim 14, characterised in that at least one of the compounds is zinc oxide and/or a precursor thereof.

16. Method for inhibiting the corrosion of glassware during washing and/or rinsing cycles of a dishwasher, characterised in that the glassware is brought in to contact with washing and/or rinsing water containing an active quantity of a composition as claimed in one of claims 8 to 12 or 14 to 15, as dependent on one of claims 8 to 12.

17. Method of inhibiting the corrosion of glassware during washing and/or rinsing cycles of a dishwasher, characterised in that a composition as claimed in claim 13 or 14 and 15, as dependent on claim 13, is placed in the interior of the dishwasher at a point accessible to the washing and/or rinsing water.

INTERNATIONAL SEARCH REPORT

Inte .onal Application No
PCT/GB 01/00910

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/12 C11D7/20 C11D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	GB 1 442 885 A (JOH A BENCKISER GMBH) 14 July 1976 (1976-07-14) page 1, line 44-83; claims 1-4	8,11-15
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P,A	WO 00 39259 A (RECKITT BENCKISER NV) 6 July 2000 (2000-07-06) page 3, paragraph 2 -page 5, paragraph 3	1-17

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

'A' document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
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European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Bertran Nadal, J

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INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/GB 01/00910

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO 00 56851 A (JOHNSON S C COMM MARKETS INC) 28 September 2000 (2000-09-28) abstract	1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte. .ional Application No
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